

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments or suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Infrastructure, Division of Program Management, 1204 Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork

0573

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE	3. REPORT TYPE AND DATES COVERED 01 Jul 2003 - 30 Jun 2004 FINAL
4. TITLE AND SUBTITLE Synthesis and Characterization of Ge Nanocrystals in Thin-Film Applications		5. FUNDING NUMBERS 63401P - 6368/2J 61102F - 2305/DX	
6. AUTHOR(S) Professor Kauzlarich			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF CALIFORNIA, DAVIS SPONSORED PROGRAMS 118 EVERSON HALL DAVIS CA 95616-5270		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NE 4015 WILSON BLVD SUITE 713 ARLINGTON VA 22203		10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-03-1-0397	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A: Unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) We have developed a new route for the synthesis of alkyl terminated Ge nanoparticles. These nanoparticles are stable and uniform in size. This is an important first step for determining how to prepare a Ge film from Ge nanoparticles. Preliminary TEM indicates that melting point of the Ge nanoparticles will be significantly lower than that of the bulk (937C). Once we know the melting point we can experiment with polymeric substrates for the preparation of Ge films with the ultimate goal of producing flexible GaAs based solar panels. These are expected to be lightweight, high power density solar panels that would be useful for space applications.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

Synthesis and Characterization of Ge Nanocrystals for thin-film Applications

Final Technical Report
Contract Number 03NE141
07/01/03 - 06/30/04

03-1-0397

Susan M. Kauzlarich
Department of Chemistry
University of California
One Shields Ave
Davis, CA 95616

Goal

This one year proposal is for the development of soluble germanium nanocrystals for the production of crystalline thin films on a non-crystalline substrate.

Introduction and Background

This proposal is for the development of a high yield synthetic route to soluble germanium nanocrystals for the production of crystalline thin films on a non-crystalline substrate. In particular, we are interested in using an organic soluble form of Ge nanoparticles that can be utilized in ink-jet technology for the production of a Ge transition layer to prepare large surface area GaAs based photovoltaics. Ge nanocrystals are the material of choice since Ge is lattice matched to GaAs and will be suitable as a substrate for GaAs-Based multijunction photovoltaics. This project is in collaboration with Dr. Donna Senft (AFRL/VSSV), Rajiv Berry (AFRL/MLBP), Giulia Galli (LLNL), Reuben Collins and Elli Sutter (CSM). This is one component of a program underway called flexible-thin-film-photovoltaics (FTFPV) within the Air Force Research Labs.

The synthesis of Ge nanoparticles has received significant attention recently with several groups making great strides in the size, shape, and surface control of these materials.¹⁻⁵ Germanium nanoparticles (np's) are of interest for many of the same reasons that silicon quantum dots are: for the study and application of the expected quantum confinement effects. In particular, Ge is attractive because of its relatively narrow bandgap and large Bohr exciton radius, making it possible to tune the photoluminescence across the visible spectrum with small changes to the particle size. In addition to the photonic properties, there are also interest in developing quantum dots such as Si and Ge for low cost film applications utilizing ink jet technologies. The fundamental idea is to have a soluble form of Ge that can be deposited into a uniform film and then recrystallized to form a single crystal substrate. The advantages of such a system are ease of fabrication, application to deposition on polymeric films, and cost. While solution methods are among the most attractive methods for preparing nanoparticles with surface derivitazation for applications such as these, there are a number of synthetic challenges. Ge np's have been synthesized in amounts necessary for powder X-ray diffraction with large numbers (>1000) of particles visible by TEM, by high temperature supercritical fluid or pressure reactions.^{3,4,6} However, this synthetic approach still has

20041119 020

challenges such as surface passivation and %yields. In addition, there are suggestions that crystalline Germanium nanoparticles can only be prepared by high temperature (greater than 400°C) or high temperature, high pressure.^{3,7} Germanium nanoparticles with functionalizable surfaces have been prepared by the metathesis of germanium containing Zintl salts with GeCl₄.^{1,8} There have been several reports of alkyl terminated Ge nanoparticles synthesized by simply reduction routes.^{2,9} The synthesis of both tetrahedrally shaped and small germanium nanoparticles by using sodium naphthalide as the reductant and *n*-butyl lithium as the terminated reagent has been reported.² This group has also been exploring reduction routes to group IV semiconductors.¹⁰⁻¹²

In this report, we show that *n*-butyl terminated crystalline Ge nanoparticles can be prepared at room temperature using sodium naphthalide as the reductant. We utilized a Grignard reagent to terminate the surface similar to our previously published work on Ge nanoparticles prepared from Zintl salts.^{1,8} In addition, we have explored the reaction parameters, such as concentration, time, and temperature, in detail and have characterized these nanoparticles by X-ray powder diffraction, transmission electron microscopy (TEM), selected area electron diffraction (SAED), high-resolution TEM (HRTEM), energy dispersive X-ray (EDX) spectroscopy, chemical analysis, FTIR, UV-vis, and fluorescence spectroscopy. Preliminary heating experiments have been performed with Eli Sutter at Colorado School of Mines (CSM).

Experimental

Materials. Ethylene glycol dimethyl ether (glyme) (Acros, 99+) was dried and distilled twice from Na-K alloy under argon. The sodium-potassium (Na-K) alloy was freshly prepared from a mixture of sodium (Aldrich, 99%) and potassium (Aldrich, 98%). Naphthalene, (C₁₀H₈) (Fisher, refined, 99.98%), germanium tetrachloride, (GeCl₄) (Acros, 99.99%), and butylmagnesium chloride (Aldrich, 2M) were used without further purification. HPLC grade water (EM Science) and HPLC grade hexane (Aldrich) was used as received. Manipulations of these chemicals were handled either in a N₂ filled glovebox or on a Schlenk line using standard anaerobic and anhydrous techniques.

Sodium Naphthalenide (Na(naph)) Synthesis. Na metal 0.5190g (0.02258 mol) was added to a Schlenk flask in a dry box and transfer to a Schlenk line. 2.894g (0.02258 mol) of naphthalene was added under Ar. ~70mL of freshly distilled and degassed glyme was added to the solids and the mixture was stir overnight. Upon dissolution of the Na metal, the solution changed from colorless to dark green.

Germanium Nanoparticle Synthesis. A 70 mL solution of Na(naph) was added rapidly via cannula to 0.70 mL (0.00602 mol) GeCl₄ in 300 mL of glyme in a Schlenk flask at room temperature. The solution immediately changed from clear to a black suspension upon the addition of the Na(naph) mixture. After 10 min. of stirring, the suspension was allowed to settle. Once settled there was a dark solid at the bottom of the flask and a deep yellow solution on top. The suspension was vacuum dried and the naphthalene was removed. Freshly distilled and degassed glyme (250 mL) was then added to the flask, followed by 3.01 mL (0.00602 mol) of n-BuMgCl. The mixture was left to stir for 12 hours. The suspension was pumped down to dryness, extracted with hexane and rinsed with acidify water. After removal of hexane and heating under

vacuum to remove any residual naphthalene, ca 500 mg of viscous yellow oil was obtained.

Variations on the Germanium Nanoparticle Synthesis. Different reaction parameters were investigated. The temperature for the initial reduction of GeCl_4 with $\text{Na}(\text{naph})$ was investigated with the Schlenk flask held at 70°C , 0°C , -40°C , and room temperature. At 0°C , reagents were added at zero degrees and warm up to room temperature, after the colloidal solution is at room temperature, the mixture was left to stir for 10 minutes. The reagents were at -40°C and left to stir until the colloidal solution is at room temperature. Reaction time was also investigated with the reaction procedure as described above, allowing the GeCl_4 and $\text{Na}(\text{naph})$ mixture to stir for 10 min, 1 hour, 2 hour, and 6 hours reaction time at room temperature. Different concentrations of $\text{Na}(\text{naph})$ in glyme (0.07593M, 0.09571M, and 0.2587M) were investigated for the same reaction time using the procedure described above. A 1-pot synthesis synthesis was also investigated. There was no removal of solvent and naphthalene before the final termination step (Grignard addition) in the 1-pot synthesis.

Characterization. Transmission electron microscopy (TEM) analyses of these nanoparticles were performed on Philips CM-12, operating at 100 keV. TEM samples were prepared by dipping the holey carbon-coated 400-mesh electron microscope grid into the hexane colloid, followed by heating in a 120°C oven overnight. Chemical analysis was obtained from Desert Analytics Laboratory in Tucson, Arizona. FTIR spectra were obtained with a Mattson Galaxy Series FTIR 3000 by either dropping the hexane colloid solution on to a NaCl plate or preparing a KBr pellet of the solid. UV-Vis spectra were obtained with a HP 8452A diode array spectrophotometer. Photoluminescence spectra of the hexane were measured on a Jobin Yvon Horiba FluoroMax-P luminescence spectrophotometer. HPLC grade hexane was used as a blank solution prior to recording each sample. Powder X-ray diffraction data were collected on an INEL CPS120 diffractometer using $\text{Cu K}\alpha_1$ radiation. In addition, Elli Sutter collected HRTEM images of Ge np on holey carbon grids at CSM as a function of temperature.

Results and Discussion

The synthesis of Ge nanoparticles by reduction of GeCl_4 or GeI_4 with Na naphthalide and with LiAlH_4 have been reported.^{2,5,9} This report explores the use of a Grignard reagent, MgClBu as the capping reagent rather than LiBu and explores the details of the reaction conditions and fully characterized the resulting product. The synthetic parameters were investigated and the resulting product examined by UV-Vis spectroscopy. In principle, the absorbance can be directly correlated to size and size distribution of the Ge nanoparticles. The results are shown in Figure 1. For most of the reactions, we used a 2 step synthetic procedure outlined in the experimental section where the solvent and naphthalene were removed prior to the addition of the Grignard reagent. In some cases, we investigated the reaction without removal of naphthalene until the very end (after addition of the Grignard) and that is referred to as the 1 pot procedure. The temperature for the initial reduction of GeCl_4 with $\text{Na}(\text{naph})$ was investigated with the Schlenk flask held at 70°C , room temperature (25°C), 0°C , and -40°C for a period of time and then MgClBu was added according to the reaction

procedure described above. Figure 1A shows the UV-vis absorbance for the product produced at the different temperatures. The absorbance is red shifted for the room temperature reaction and almost the same for both the high and low temperatures. However, the absorbance is blue shifted for the reaction run at 0°C. In addition, the room temperature reaction product shows a more gradual slope in absorbance compared to the high and low temperature spectra. These observations are consistent with the average size of the nanoparticles being largest for the room temperature reaction and almost the same for both the high and low temperature reactions. The correlation of the absorption spectrum with size of the nanoparticles produced can be verified by TEM and TEM is consistent with those conclusions. The room temperature reaction produced nanoparticles with average diameter of 7.4 (2.3) based on 1000 particles and the high temperature reaction was approximately 11.0 (2.7) based on 1000 particles. These results suggest that nucleation of the nanoparticles occurs immediately for either the high or low temperature reaction, but that the room temperature reaction allows for nucleation at various times.

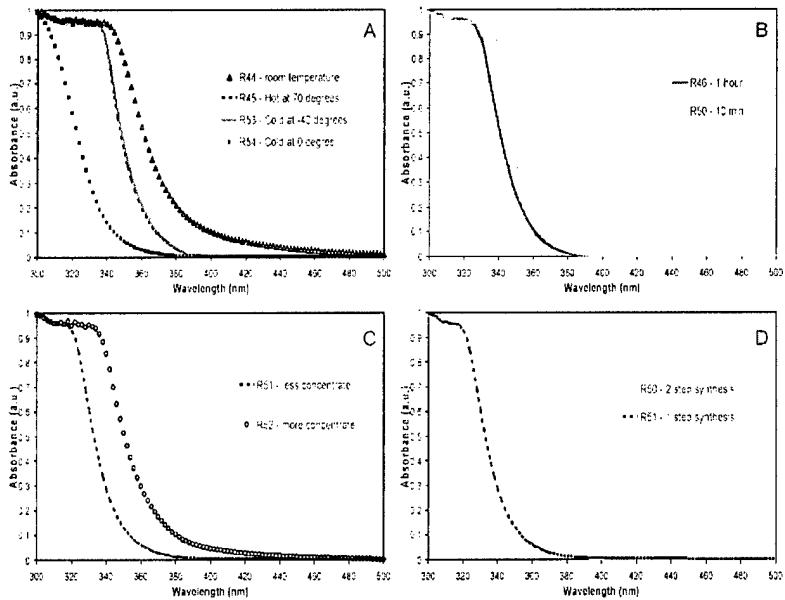


Figure 1. Absorption spectra of Ge np terminated with butyl produced from reduction (A) at temperatures of -40, 0, 25, and 70°C as a function of temperature dependence, (B) as a function of reaction time (10 min, 1 hour), (C) as a function of concentration of Na(naphth), and (D) 1 step versus 2 steps synthesis.

In order to explore the growth of the nanoparticles, time for the reaction to proceed was also investigated. Figure 1B shows the absorption spectra for the product resulting from different reaction times for the GeCl_4 and Na(naphth) mixture to stir, either 10 min or 1 hour prior to the addition of the Grignard reagent. No significant differences in absorbance can be seen suggesting that the nanoparticles do not continue to grow after the initial nucleation event. The average diameter of the nanoparticles obtain from the reactions was 4.6 (1.4) for the 1 hour reaction and 5.0 (1.0) for the 10 min reaction based on approximately 1000 particles for each reaction. Under these synthetic conditions, the

reaction is complete within the first 10 minutes and particles do not continue to grow at room temperature. Since these reactions are run so that chlorine is always left on the surface of the particle, it is possible that this provides a passivated surface that does not continue to react.

Relative stoichiometry may play an important role as well; however, we chose to keep the stoichiometry (mole ratio) the same and explore the effect of concentration. Concentrations of Na(naphth) in glyme (0.07593M, 0.09571M) were investigated for the 1 hour synthesis, and the 10 minute 1 pot synthesis. Figure 1C shows the product resulting from the 1 hour synthesis, however; the results from the 10 min 1 pot synthesis followed the same trend. The spectra are consistent with the more concentrated solution producing slightly larger sized nanoparticles and the less concentrated solution producing smaller sized nanoparticles. The average diameter of the more concentrated solution was 6.5 (2.0) based on 1136 particles whereas the less concentrated reaction produced nanoparticles of average diameter 6.1 (2.0) based on 712 particles. In addition, it was noted that the product from the 1 pot synthetic procedure results in a slightly smaller average size nanoparticle for the synthetic procedure which removes the naphthalene for the same concentration and stoichiometry. This is shown in Figure 1D where the product of the normal synthetic procedure produces an absorption that is red shifted compared to that of the 1 pot procedure. This is not surprising since the mixture must be heated in the normal procedure to remove the solvent and naphthalene.

Overall, based on the absorbance spectra of the various products and their corresponding TEM's, we can conclude that nucleation can be controlled by temperature and at temperatures other than room temperature; the nanoparticles quickly achieve their maximum size based on concentration and stoichiometry. Longer times (1 hour vs 10 min at room temperature) do not appear to result in drastically different average sized nanoparticles.

Figures 2A and 2B are the bright and dark field microscopy images of Ge nanoparticles prepared from a normal synthesis at room temperature. Figures 2C and 2D are the bright and dark field microscopy images of Ge nanoparticles prepared from a 1 pot synthesis at room temperature. Figures 3A is a bright field microscopy image of a normal synthesis with the histogram of sizes. Figure 3B is a bright field microscopy image of 1 pot synthesis with the histogram of size distributions. Figure 3C is a bright field microscopy image of a 1 step synthesis with higher concentration and the size distribution is shown in the image. EDX of all samples confirmed the presence of Ge, C, H, Cl, with little or no Na present. The presence of chloride was further investigated with chemical analysis.

The elemental analysis of the product after the reaction of GeCl_4 with Na(naphth) with subsequent removal of solvent and napthalene is consistent with a chloride terminated Ge np's of approximate stoichiometry: $\text{Ge}_{4\text{Cl}_{0.5}} + 1.75\text{NaCl} + \text{C}_{0.6}\text{H}_{1.5}\text{O}_{3.4}$. In addition to the Ge np, NaCl is present and also a small amount of organic that can be attributed to either the glyme solvent or a small amount of napthalene. After this product is terminated with butyl magnesium chloride, extracted into hexane and washed with water, the percentage mole ratio of the isolated yellow oil was $\text{Ge}_4(\text{C}_4\text{H}_9) + \text{C}_{39}\text{H}_{85}\text{O}_1 +$

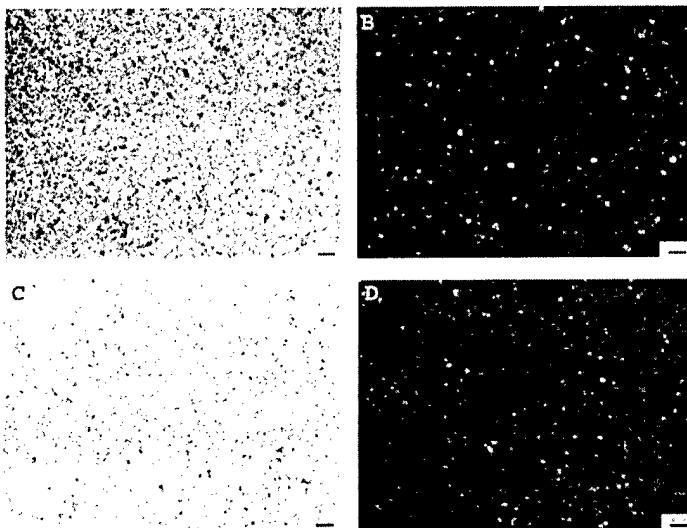


Figure 2. (A) Bright field and (B) dark field microscopy image (100 keV) of the product from a 2 step synthesis. (C) Bright field and (D)

0.018NaCl. These results are consistent with the removal of salt or naphthalene from the final product after the workup step and the chloride is replaced by the butyl group on the surface. In a 1 pot reaction, with higher concentration reaction, the elemental analysis showed Ge:C:H (4:54.54:100.61). This would be consistent with $\text{Ge}_4(\text{C}_4\text{H}_9) + \text{C}_{50}\text{H}_{91}$. The carbon and hydrogen content in both samples is suggestive of the presence of a hydrocarbon polymeric material in the final product. This side product may be controlled by the nature of the reductant, the solvent, or the temperature. This is currently being investigated.

FTIR provide evidence for the organic moieties present in the product. FTIR (not shown) contain 4 peaks at 2956, 2926, 2871, 2857 cm^{-1} , characteristic C-H stretches of the terminated methyl stretching modes, indicated the presence of $-\text{CH}_2-$ and $-\text{CH}_3$ groups on the surface of Ge nanoparticles. Peaks at 1376 and 1463 cm^{-1} are also observed and are the symmetric and asymmetric bends of the methyl group. The alkyl termination prevents oxidation of the particles and provides a stable passivation layer.

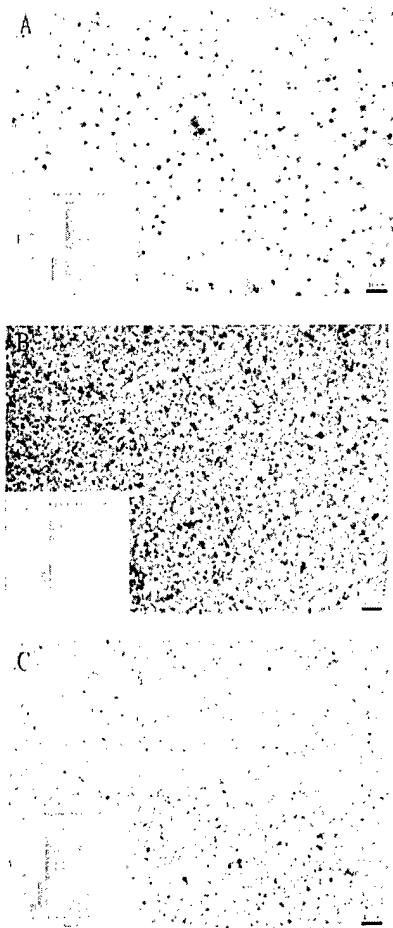


Figure 3. (A) Bright field image and histogram for a 2-pot synthesis. (B) Bright field image and histogram for a 1-pot synthesis. (C) Bright field image and histogram for a concentrated 1-pot synthesis.

These nanoparticles have been characterized with a heating stage by Eli Sutter (CSM). The preliminary data suggests that the nanoparticles aggregate and grow at temperatures as low as 300°C.

Acknowledgements: We thank Richard Baldwin for his initial work on this project, Professor Frank Osterloh for useful discussion. This research has been funded in part by Evergreen Solar by means of a NIST ATP grant, NSF DMR-0120990, CHE-0304871 and AFOSR-03NE141 .

Accomplishments/New Findings: We have developed a new route for the synthesis of alkyl terminated Ge nanoparticles. These nanoparticles are stable and uniform in size. This is an important first step for determining how to prepare a Ge film from Ge nanoparticles. Preliminary TEM indicates that melting point of the Ge nanoparticles will be significantly lower than that of the bulk (937°C). Once we know the melting point we can experiment with polymeric substrates for the preparation of Ge films with the ultimate goal of producing flexible GaAs based solar panels. These are expected to be lightweight, high power density solar panels that would be useful for space applications.

Personnel Supported: Ivy Hsiang Wei Chiu, graduate student

Publications: "Facile Synthesis of Alkyl Terminated Ge nanocrystals" Ivy Hsiang Wei Chiu, and Susan M. Kauzlarich, in preparation.

Interactions/Transitions:

- (a) none at this time.
- (b) none at this time.

(c) Donna Senft at (AFRL/VSSV) has provided useful discussion. Eli Sutter and Reuben Colin (Colorado School of Mines) are also involved in the characterization of these nanoparticles.

New Discoveries, inventions, or patent disclosures: none at this time.

Honors/Awards: None

- (1) Taylor, B. R.; Fox, G. A.; Hope-Weeks, L. J.; Maxwell, R. S.; Kauzlarich, S. M.; Lee, H. W. H. *Mater Sci Eng* **2002**, *B96*, 90-93.
- (2) Hope-Weeks, L. J. *Chem. Comm.* **2003**, 2980-2981.
- (3) Gerion, D.; Zaitseva, N.; Saw, C.; Casula, M. F.; Fakra, S.; Van Buuren, T.; Galli, G. *Nano Letters* **2004**, *4*, 597-602.
- (4) Lu, X.; Ziegler, K. J.; Ghezelbash, A.; Johnston, K. P.; Korgel, B. A. *Nano Letters* **2004**, *4*, 969-974.
- (5) Fok, E.; Shih, M.; Meldrum, A.; Veinot, J. G. C. *Chem. Commun.* **2004**, 386-387.
- (6) Heath, J. R.; Shiang, J. J.; Alivisatos, A. P. *J. Chem. Phys.* **1994**, *101*, 1607-1615.
- (7) Lu, X.; Ziegler, K. J.; Ghezelbash, A.; Johnston, K. P.; Korgel, B. A. *Nano Letters* **2004**, *4*, 969-874.
- (8) Tanke, R. S.; Kauzlarich, S. M.; Patten, T. E.; Pettigrew, K. A.; Murphy, D. L.; Thompson, M. E.; Lee, H. W. H. *Chem Mater* **2003**, *15*, 1682-1689.
- (9) Wilcoxon, J. P.; Provencio, P. P.; Samara, G. A. *Phys Rev B* **2001**, *64*, 035417-035419.
- (10) Baldwin, R. K.; Pettigrew, K. A.; Ratai, E.; Augustin, M. P.; Kauzlarich, S. M. *Chem. Comm.* **2002**, 1822-1823.
- (11) Baldwin, R. K.; Pettigrew, K. A.; Garno, J. C.; Power, P. P.; Liu, G. Y.; Kauzlarich, S. M. *J Am Chem Soc* **2002**, *124*, 1150-1151.
- (12) Zou, J.; Baldwin, R. K.; Pettigrew, K. A.; Kauzlarich, S. M. *Nano Letters* **2004**, *4*, 1181-1186.